

10/849,696

STM-STRUCTURE SEARCH
10/19-04

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L5 ANSWER 1 OF 16 CAPLUS COPYRIGHT 2004 ACS on STN
ACCESSION NUMBER: 2003:466693 CAPLUS
DOCUMENT NUMBER: 139:36672
TITLE: Preparation of codeine from morphine
INVENTOR(S): Hill, Lloyd P.
PATENT ASSIGNEE(S): Mallinckrodt Inc., USA
SOURCE: U.S., 4 pp.
CODEN: USXXAM
DOCUMENT TYPE: Patent
LANGUAGE: English
FAMILY ACC. NUM. COUNT: 1
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
US 6579985	B1	20030617	US 2002-274702	20021021
WO 2004037826	A2	20040506	WO 2003-US32698	20031014
WO 2004037826	A3	20040701		

W: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW, AM, AZ, BY, KG, KZ, MD, RU

RW: GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO, SE, SI, SK, TR, BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG

PRIORITY APPLN. INFO.: US 2002-274702 A 20021021

OTHER SOURCE(S): CASREACT 139:36672

AB An improved process for the preparation of codeine from morphine comprises the steps of (a) reacting morphine with a methylating agent in the presence of a hydrocarbon solvent at a temperature of 100 to 215° C. under reflux conditions such that approx. 50% or more of the hydrocarbon solvent is returned to the reaction mixture to substantially avoid the formation of codeine Me ether; and (b) recovering codeine from the reaction mixture. The process may include step (a) above followed by (b) cooling the reaction mixture to approx. 85° C. and adding water to terminate the reaction; (c) raising the pH of the reaction mixture to approx. 11; (d) separating the hydrocarbon solvent phase containing codeine and dimethylaniline; and (e) adding a dilute mineral or organic acid and approx. 6 to 7 times the volume of water for each volume of hydrocarbon solvent to sep. dimethylaniline and codeine.

IT 76-57-3P, Codeine

RL: IMF (Industrial manufacture); SPN (Synthetic preparation); **PREP**
(Preparation)

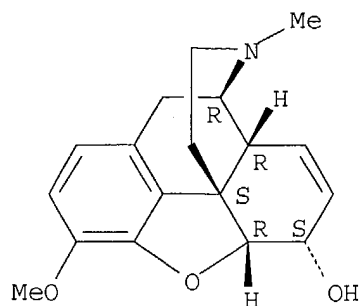
(process for preparation of codeine from morphine)

RN 76-57-3 CAPLUS

CN Morphinan-6-ol, 7,8-didehydro-4,5-epoxy-3-methoxy-17-methyl-,
(5 α ,6 α)- (9CI) (CA INDEX NAME)

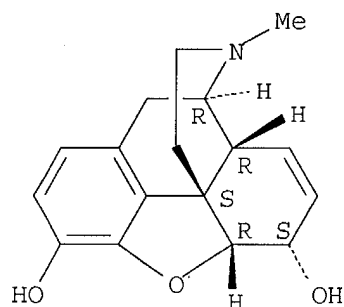
Absolute stereochemistry.

10/849,696



IT 57-27-2, Morphine, reactions
RL: **RCT (Reactant)**; RACT (Reactant or reagent)
(process for preparation of codeine from morphine)
RN 57-27-2 CAPLUS
CN Morphinan-3,6-diol, 7,8-didehydro-4,5-epoxy-17-methyl-
(5 α ,6 α) - (9CI) (CA INDEX NAME)

Absolute stereochemistry. Rotation (-).



REFERENCE COUNT: 2 THERE ARE 2 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L5 ANSWER 2 OF 16 CAPLUS COPYRIGHT 2004 ACS on STN
ACCESSION NUMBER: 2002:946115 CAPLUS
DOCUMENT NUMBER: 138:16594
TITLE: Sustained-release analgesic compounds
INVENTOR(S): Ashton, Paul; Smith, Thomas J.; Cynkowski, Tadeusz;
Cynkowska, Grazyna; Mickunas, Edmund
PATENT ASSIGNEE(S): Control Delivery Systems, USA
SOURCE: PCT Int. Appl., 54 pp.
CODEN: PIXXD2
DOCUMENT TYPE: Patent
LANGUAGE: English
FAMILY ACC. NUM. COUNT: 1
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
WO 2002098427	A2	20021212	WO 2002-US17613	20020605
WO 2002098427	A3	20030220		

W: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TN, TR, TT, TZ,

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UA, UG, UZ, VN, YU, ZA, ZM, ZW, AM, AZ, BY, KG, KZ, MD, RU, TJ, TM
RW: GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW, AT, BE, CH,
CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR,
BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG
US 2003022876 A1 20030130 US 2002-162216 20020605
NZ 529661 A 20031219 NZ 2002-529661 20020605
EP 1399161 A2 20040324 EP 2002-734669 20020605
R: AT, BE, CH, DE, DK, ES, FR, GB, GR, IT, LI, LU, NL, SE, MC, PT,
IE, SI, LT, LV, FI, RO, MK, CY, AL, TR
BR 2002010179 A 20040427 BR 2002-10179 20020605
PRIORITY APPLN. INFO.: US 2001-295556P P 20010605
WO 2002-US17613 W 20020605

OTHER SOURCE(S): MARPAT 138:16594

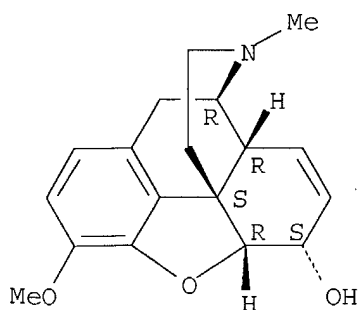
AB A pharmaceutically active inventive compound comprises two independently active analgesic moieties covalently conjoined through a physiol. labile linker. A preferred embodiment comprises an opioid, such as morphine, covalently linked to at least one analgesic compound selected from the group consisting of an opioid or a no-opioid compound through a physiol. labile linker. Suitable covalent linkers are covalently bonded to the two independently active analgesic compds. through one or more lactone, lactam, or sulfonamido linkages. Suitable linkers include endogenous carboxylate, amido, and sulfonamido moieties, and exogenous moieties that form the aforementioned lactone, lactam or sulfonamido linkages.

IT **76-57-3DP**, Codeine, conjugates with analgesics
RL: PAC (Pharmacological activity); SPN (Synthetic preparation); THU (Therapeutic use); BIOL (Biological study); **PREP (Preparation)**;
USES (Uses)
(sustained-release analgesic compds.)

RN 76-57-3 CAPLUS

CN Morphinan-6-ol, 7,8-didehydro-4,5-epoxy-3-methoxy-17-methyl-,
(5 α ,6 α)- (9CI) (CA INDEX NAME)

Absolute stereochemistry.

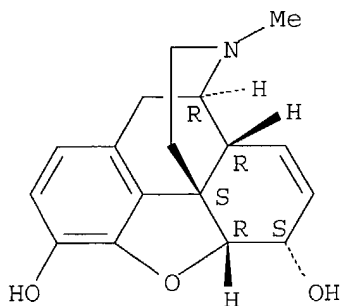


IT **57-27-2**, Morphine, reactions
RL: **RCT (Reactant)**; RACT (Reactant or reagent)
(sustained-release analgesic compds.)

RN 57-27-2 CAPLUS

CN Morphinan-3,6-diol, 7,8-didehydro-4,5-epoxy-17-methyl-,
(5 α ,6 α)- (9CI) (CA INDEX NAME)

Absolute stereochemistry. Rotation (-).

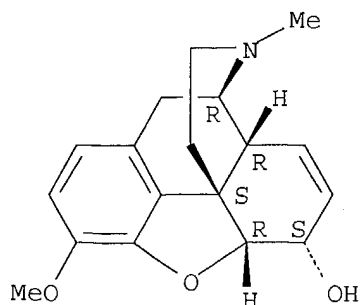


L5 ANSWER 3 OF 16 CAPLUS COPYRIGHT 2004 ACS on STN
 ACCESSION NUMBER: 2002:276043 CAPLUS
 DOCUMENT NUMBER: 136:295249
 TITLE: Resin and its use in converting morphine to codeine
 INVENTOR(S): Corcoran, Robert C.
 PATENT ASSIGNEE(S): USA
 SOURCE: PCT Int. Appl., 58 pp.
 CODEN: PIXXD2
 DOCUMENT TYPE: Patent
 LANGUAGE: English
 FAMILY ACC. NUM. COUNT: 1
 PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
WO 2002028917	A2	20020411	WO 2001-US31252	20011005
WO 2002028917	A3	20020926		
W: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PH, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW, AM, AZ, BY, KG, KZ, MD, RU, TJ, TM				
RW: GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW, AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR, BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG				
AU 2001096651	A5	20020415	AU 2001-96651	20011005
US 2002082357	A1	20020627	US 2001-970860	20011005
PRIORITY APPLN. INFO.:			US 2000-238697P	P 20001006
			WO 2001-US31252	W 20011005
AB A resin, useful as a methylating agent, comprises a solid support and cationic methylated sulfonium, sulfoxonium, selenonium or phosphonium salts immobilized on the solid support. Amberlite A 26 (hydroxide form) was mixed with 3-methylthiophenol, heated in xylene, MeOH and dimethylsulfate was added, the resin was washed in aqueous NaCl and aqueous NaOH,				
and rinsed with MeOH to give methylsulfonium methylation resin in its hydroxide/methoxide form.				
IT 76-57-3P, Codeine				
RL: IMF (Industrial manufacture); PUR (Purification or recovery);				
PREP (Preparation)				
(methylation resin for converting morphine to codeine)				
RN 76-57-3 CAPLUS				
CN Morphinan-6-ol, 7,8-didehydro-4,5-epoxy-3-methoxy-17-methyl-, (5 α ,6 α)- (9CI) (CA INDEX NAME)				

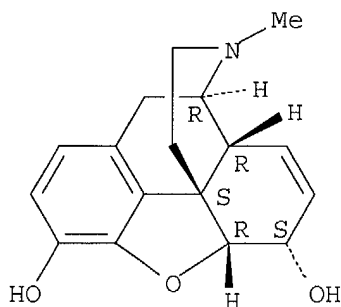
Absolute stereochemistry.

10/849,696



IT 57-27-2, Morphine, reactions
RL: **RCT (Reactant)**; RACT (Reactant or reagent)
(methylation resin for converting morphine to codeine)
RN 57-27-2 CAPLUS
CN Morphinan-3,6-diol, 7,8-didehydro-4,5-epoxy-17-methyl-
(5 α ,6 α) - (9CI) (CA INDEX NAME)

Absolute stereochemistry. Rotation (-).



L5 ANSWER 4 OF 16 CAPLUS COPYRIGHT 2004 ACS on STN
ACCESSION NUMBER: 1997:453959 CAPLUS
DOCUMENT NUMBER: 127:65986
TITLE: Solid-phase synthesis of codeine from morphine
INVENTOR(S): Corcoran, Robert C.; Ma, Junning
PATENT ASSIGNEE(S): Board of Regents of the University and Community
College System of Nevada, USA; Corcoran, Robert C.;
Ma, Junning
SOURCE: PCT Int. Appl., 14 pp.
CODEN: PIXXD2
DOCUMENT TYPE: Patent
LANGUAGE: English
FAMILY ACC. NUM. COUNT: 1
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
WO 9719082	A1	19970529	WO 1996-US18791	19961121
W:	AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, HU, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TR, TT, UA, UG, US, UZ, VN, AM, AZ, BY, KG, KZ, MD, RU, TJ, TM			
RW:	KE, LS, MW, SD, SZ, UG, AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, BF, BJ, CF, CG, CI, CM, GA, GN, ML,			

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MR, NE, SN, TD, TG

US 5981750	A	19991109	US 1996-753040	19961119
AU 9711624	A1	19970611	AU 1997-11624	19961121
IN 186312	A	20010804	IN 1996-DE2564	19961121
US 6204337	B1	20010320	US 1999-390285	19990903
PRIORITY APPLN. INFO.:			US 1995-7419P	P 19951121
			US 1996-753040	A3 19961119
			WO 1996-US18791	W 19961121

OTHER SOURCE(S): CASREACT 127:65986

AB A methylation resin comprising methyl(dialkyl)anilinium salts or methyl(diaryl)anilinium salts covalently bonded to the resin was prepared and used in the solid-phase synthesis of codeine from morphine. Accordingly, the specification describes a process for methylating morphine to form codeine by loading morphine onto a methylation resin comprising methyl(dialkyl)anilinium salts or methyl(diaryl)anilinium salts covalently bonded to the resin; contacting the loaded resin with sufficient hydrocarbon or ether solvent to cover the loaded resin; and heating the loaded resin in the hydrocarbon or ether solvent under sufficient conditions to form codeine. The methylating resin may be used to methylate phenolic moieties on other compds. and to esterify compds. containing carboxylic acid moieties.

IT 76-57-3P, Codeine

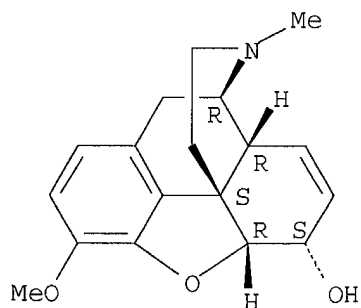
RL: IMF (Industrial manufacture); SPN (Synthetic preparation); **PREP** (Preparation)

(solid-phase synthesis of codeine from morphine)

RN 76-57-3 CAPLUS

CN Morphinan-6-ol, 7,8-didehydro-4,5-epoxy-3-methoxy-17-methyl-, (5 α ,6 α)- (9CI) (CA INDEX NAME)

Absolute stereochemistry.



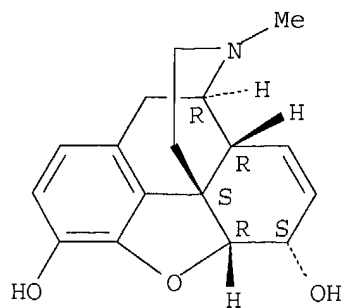
IT 57-27-2, Morphine, reactions

RL: **RCT (Reactant)**; RACT (Reactant or reagent)
(solid-phase synthesis of codeine from morphine)

RN 57-27-2 CAPLUS

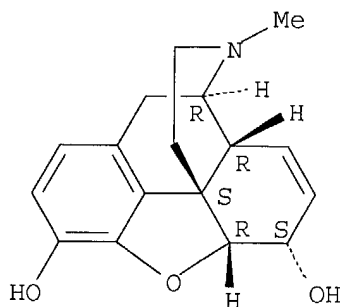
CN Morphinan-3,6-diol, 7,8-didehydro-4,5-epoxy-17-methyl-, (5 α ,6 α)- (9CI) (CA INDEX NAME)

Absolute stereochemistry. Rotation (-).



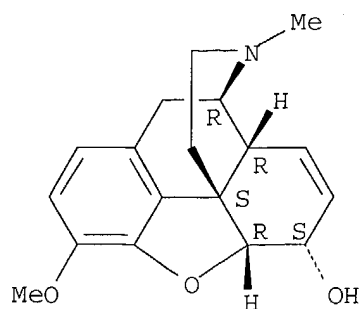
L5 ANSWER 5 OF 16 CAPLUS COPYRIGHT 2004 ACS on STN
 ACCESSION NUMBER: 1996:717793 CAPLUS
 DOCUMENT NUMBER: 126:19081
 TITLE: Preparation of phenyltrimethylammonium chloride
 AUTHOR(S): Nguyen, Huu Dinh
 CORPORATE SOURCE: Hanoi, Vietnam
 SOURCE: Hoa Hoc & Cong Nghiep Hoa Chat (1996), (1), 22-24
 CODEN: HHHCF4; ISSN: 0866-7004
 PUBLISHER: Hoi Hoa Hoc Viet Nam
 DOCUMENT TYPE: Journal
 LANGUAGE: Vietnamese
 AB PhN+Me3 Cl⁻ was prepared in 78% yield by reaction of PhNMe₂ with MeCl in absolute ethanol at 120° C under 20-25 atm during 12 h. The product was used to methylate morphine to codeine.
 IT **57-27-2**, Morphine, reactions
 RL: **RCT (Reactant)**; RACT (Reactant or reagent)
 (preparation of phenyltrimethylammonium chloride for methylation of morphine)
 RN 57-27-2 CAPLUS
 CN Morphinan-3,6-diol, 7,8-didehydro-4,5-epoxy-17-methyl-, (5α,6α)- (9CI) (CA INDEX NAME)

Absolute stereochemistry. Rotation (-).



IT **76-57-3P**, Codeine
 RL: SPN (Synthetic preparation); **PREP (Preparation)**
 (preparation of phenyltrimethylammonium chloride for methylation of morphine)
 RN 76-57-3 CAPLUS
 CN Morphinan-6-ol, 7,8-didehydro-4,5-epoxy-3-methoxy-17-methyl-, (5α,6α)- (9CI) (CA INDEX NAME)

Absolute stereochemistry.



L5 ANSWER 6 OF 16 CAPLUS COPYRIGHT 2004 ACS on STN
 ACCESSION NUMBER: 1994:483714 CAPLUS
 DOCUMENT NUMBER: 121:83714
 TITLE: Process for purifying codeine prepared by methylation of morphine
 INVENTOR(S): Kmetty, Gejza; Varga, Ivan; Kacina, Roman; Gomory, Juraj
 PATENT ASSIGNEE(S): SLOVAKOFARMA s. p., Slovakia
 SOURCE: Czech., 3 pp.
 CODEN: CZXXA9
 DOCUMENT TYPE: Patent
 LANGUAGE: Slovak
 FAMILY ACC. NUM. COUNT: 1
 PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
CS 277517	B6	19930317	CS 1990-6197	19901212

PRIORITY APPLN. INFO.: CS 1990-6197 19901212

AB Codeine (I), prepared by methylation of morphine, is freed of known contaminants as follows. A solution of crude I in an organic solvent (especially PhMe) is extracted by an aqueous solution of an inorg. or a Cl-2 organic acid (pH 5.4-7, preferably 6.0-6.8), and then the separated aqueous layer containing I is extracted with a chlorinated organic solvent (especially C₂HCl₃). I base is then precipitated from the aqueous layer by raising the pH to 8-9, and after separation from the layer is dissolved in EtOH and treated with aqueous or aqueous-alc. H₃PO₄ to pH 4-4.5.

The resulting crystalline I phosphate is separated, and from it is liberated pure I base. In a large-scale example, 35 kg I crude base in PhMe was extracted into aqueous 3.5% formic acid, which was then extracted with C₂HCl₃, treated with active C, and neutralized to precipitate 32 kg I base, free of methylation byproducts. This was dissolved in EtOH and treated with aqueous 40% H₃PO₄, to give crystalline I.H₃PO₄ satisfying German pharmacopeial parameters for purity and solution color, with content 99.95%.

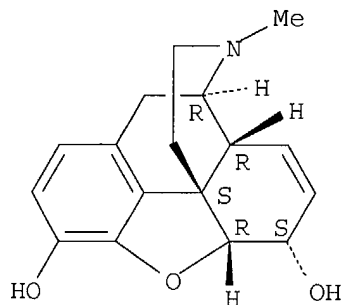
IT 57-27-2, Morphine, reactions
 RL: **RCT (Reactant)**; RACT (Reactant or reagent)
 (methylation of, purification of codeine from)

RN 57-27-2 CAPLUS

CN Morphinan-3,6-diol, 7,8-didehydro-4,5-epoxy-17-methyl-
 (5α,6α)- (9CI) (CA INDEX NAME)

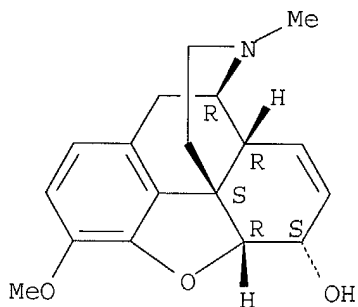
Absolute stereochemistry. Rotation (-).

10/849,696



IT **76-57-3P**, Codeine
RL: PUR (Purification or recovery); **PREP (Preparation)**
(purification of, from methylation of morphine)
RN 76-57-3 CAPLUS
CN Morphinan-6-ol, 7,8-didehydro-4,5-epoxy-3-methoxy-17-methyl-,
(5 α ,6 α) - (9CI) (CA INDEX NAME)

Absolute stereochemistry.



L5 ANSWER 7 OF 16 CAPLUS COPYRIGHT 2004 ACS on STN
ACCESSION NUMBER: 1994:164598 CAPLUS
DOCUMENT NUMBER: 120:164598
TITLE: Semisynthesis of codeine
AUTHOR(S): Phan, Dinh Chau; Do, Hiru Nghi
CORPORATE SOURCE: Ha Noi Pharm. Univ., Vietnam
SOURCE: Tap Chi Duoc Hoc (1993), (4), 15-16
CODEN: TCDHDQ; ISSN: 0258-6967
DOCUMENT TYPE: Journal
LANGUAGE: Vietnamese

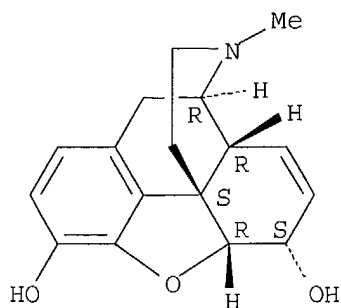
AB Codeine (I) was prepared in 75 - 85% yield by methylation of the phenolic OH group of morphine with trimethylphenylammonium arylsulfonate. The quality of I meets all the stds. of the Vietnamese Pharmacopeia.

IT **57-27-2**, Morphine, reactions
RL: **RCT (Reactant)**; RACT (Reactant or reagent)
(methylation of)

RN 57-27-2 CAPLUS
CN Morphinan-3,6-diol, 7,8-didehydro-4,5-epoxy-17-methyl-,
(5 α ,6 α) - (9CI) (CA INDEX NAME)

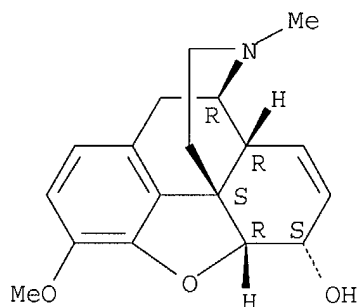
Absolute stereochemistry. Rotation (-).

10/849,696



IT **76-57-3P**, Codeine
RL: SPN (Synthetic preparation); **PREP (Preparation)**
(preparation of, method for)
RN 76-57-3 CAPLUS
CN Morphinan-6-ol, 7,8-didehydro-4,5-epoxy-3-methoxy-17-methyl-,
(5 α ,6 α) - (9CI) (CA INDEX NAME)

Absolute stereochemistry.



L5 ANSWER 8 OF 16 CAPLUS COPYRIGHT 2004 ACS on STN

ACCESSION NUMBER: 1990:198876 CAPLUS

DOCUMENT NUMBER: 112:198876

TITLE: An improved process for the preparation of codeine from morphine

INVENTOR(S): Ayyangar, Nagaraj Ramanuj; Choudhary, Anil Ramkumar; Kalkote, Uttam Ramrao; Sharma, Vasant Kaushal

PATENT ASSIGNEE(S): Council of Scientific and Industrial Research, India

SOURCE: Indian, 10 pp.

CODEN: INXXAP

DOCUMENT TYPE: Patent

LANGUAGE: English

FAMILY ACC. NUM. COUNT: 1

PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
IN 164587	A	19890415	IN 1986-DE109	19860205

PRIORITY APPLN. INFO.: IN 1986-DE109 19860205

AB Codeine (I), useful as an analgesic and antitussive, is prepared by methylation of morphine (II) with PhNMe₃ Cl⁻ (III) in the presence of alkali metal carbonate in a hydrocarbon solvent at 45-120°. II of very low purity of 30 to 95% containing gums and resins can be directly used for the process and the yield of I is quant. and therefore the process minimizes the production cost. Thus, II (89.0% purity) 320, K₂CO₃ 552 and III

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188 parts were heated 2-5 h at 45-120° under stirring in PhMe. The reaction mixture was filtered, PhMe distilled off, acidified to pH 5-5.5, and steam-distilled to remove PhNMC2. On basification I (99% purity) was separated in 99% yield.

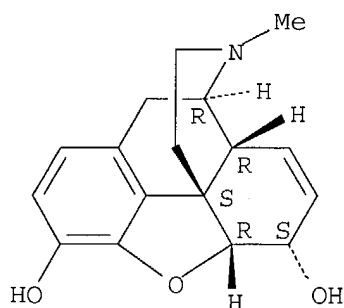
IT 57-27-2, Morphine, reactions

RL: **RCT (Reactant)**; RACT (Reactant or reagent)
(methylation of, by trimethylphenylammonium chloride)

RN 57-27-2 CAPLUS

CN Morphinan-3,6-diol, 7,8-didehydro-4,5-epoxy-17-methyl-
(5 α ,6 α) - (9CI) (CA INDEX NAME)

Absolute stereochemistry. Rotation (-).



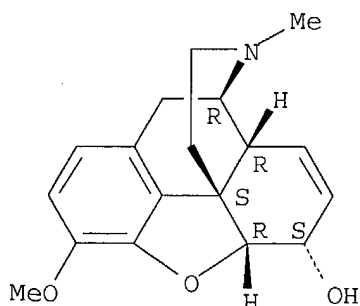
IT 76-57-3P, Codeine

RL: SPN (Synthetic preparation); **PREP (Preparation)**
(prepn of, by methylation of morphine with trimethylphenylammonium chloride)

RN 76-57-3 CAPLUS

CN Morphinan-6-ol, 7,8-didehydro-4,5-epoxy-3-methoxy-17-methyl-,
(5 α ,6 α) - (9CI) (CA INDEX NAME)

Absolute stereochemistry.



L5 ANSWER 9 OF 16 CAPLUS COPYRIGHT 2004 ACS on STN

ACCESSION NUMBER: 1989:24125 CAPLUS

DOCUMENT NUMBER: 110:24125

TITLE: Improved process for the preparation of codeine from morphine

INVENTOR(S): Ayyangar, Nagaraj Ramanuj; Choudhary, Anil Ramkumar; Kalkote, Uttam Ramrao; Sharma, Vasant Kaushal

PATENT ASSIGNEE(S): Council of Scientific and Industrial Research, India

SOURCE: Eur. Pat. Appl., 6 pp.

CODEN: EPXXDW

DOCUMENT TYPE: Patent

LANGUAGE: English

10/849,696

FAMILY ACC. NUM. COUNT: 1

PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
EP 268710	A1	19880601	EP 1986-309180	19861125
EP 268710	B1	19910515		
R: AT, CH, DE, FR, GB, LI, NL				
AT 63554	E	19910615	AT 1986-309180	19861125
US 4764615	A	19880816	US 1986-940517	19861210
PRIORITY APPLN. INFO.:			EP 1986-309180	19861125

OTHER SOURCE(S): CASREACT 110:24125

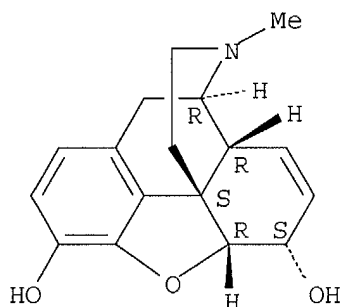
AB Codeine (I) was prepared from morphine (II) by reaction with Me₃PhN⁺ Cl⁻ in the presence of an alkali metal carbonate and a hydrocarbon solvent at 45-120°. II (35% purity), K₂CO₃, and Me₃PhN⁺ Cl⁻ were stirred 2-5 h in PhMe at 45-120° to give 99% I.

IT 57-27-2, Morphine, reactions
RL: **RCT (Reactant)**; RACT (Reactant or reagent)
(methylation of, by trimethylphenylammonium chloride)

RN 57-27-2 CAPLUS

CN Morphinan-3,6-diol, 7,8-didehydro-4,5-epoxy-17-methyl-
(5 α ,6 α)- (9CI) (CA INDEX NAME)

Absolute stereochemistry. Rotation (-).

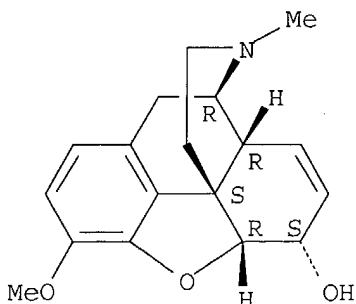


IT 76-57-3P, Codeine
RL: SPN (Synthetic preparation); **PREP (Preparation)**
(preparation of)

RN 76-57-3 CAPLUS

CN Morphinan-6-ol, 7,8-didehydro-4,5-epoxy-3-methoxy-17-methyl-,
(5 α ,6 α)- (9CI) (CA INDEX NAME)

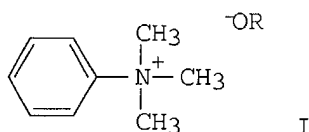
Absolute stereochemistry.



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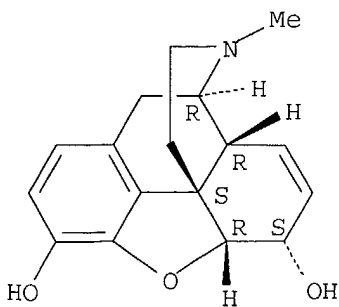
ACCESSION NUMBER: 1988:438019 CAPLUS
DOCUMENT NUMBER: 109:38019
TITLE: Preparation of codeine by methylation of morphine
INVENTOR(S): Snuparek, Vladislav
PATENT ASSIGNEE(S): Czech.
SOURCE: Czech., 3 pp.
CODEN: CZXXA9
DOCUMENT TYPE: Patent
LANGUAGE: Slovak
FAMILY ACC. NUM. COUNT: 1
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
CS 235590	B1	19850515	CS 1983-7601	19831017
PRIORITY APPLN. INFO.:			CS 1983-7601	19831017
OTHER SOURCE(S):	CASREACT	109:38019		
GI				



- AB Codeine is prepared by methylation of morphine with the quaternary ammonium compound I (R = H, Me, Et). A 10-50 weight% solution of I in MeOH or EtOH is added to a suspension of morphine in xylene preheated to 110-125°, temperature is maintained at 100-115°, and the reaction is finished by heating to 115°. The procedure is suitable for industrial manufacture of codeine, an antitussive. Morphine was suspended in 1000 mL xylene and the stirred suspension was heated at 115° whereupon a solution of 88.6 g I (R = H) in 220 mL MeOH was gradually added during 90 min at 105-110° followed by heating at 115° to give 98% codeine.
- IT 57-27-2, Morphine, reactions
RL: **RCT (Reactant)**; RACT (Reactant or reagent)
(methylation of, with phenyltrimethylammonium salt)
- RN 57-27-2 CAPLUS
- CN Morphinan-3,6-diol, 7,8-didehydro-4,5-epoxy-17-methyl-
(5 α ,6 α) - (9CI) (CA INDEX NAME)

Absolute stereochemistry. Rotation (-).

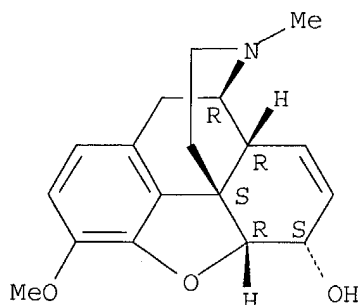


- IT 76-57-3P, Codeine
RL: SPN (Synthetic preparation); **PREP (Preparation)**
(preparation of, by methylation of morphine)

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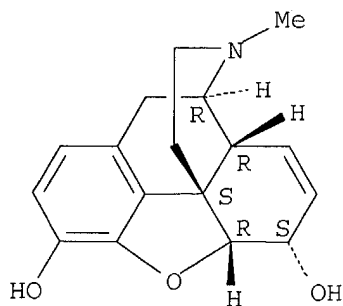
RN 76-57-3 CAPLUS
CN Morphinan-6-ol, 7,8-didehydro-4,5-epoxy-3-methoxy-17-methyl-,
(5 α ,6 α)- (9CI) (CA INDEX NAME)

Absolute stereochemistry.



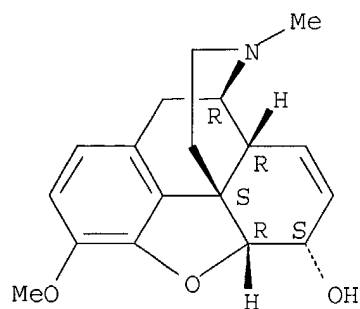
L5 ANSWER 11 OF 16 CAPLUS COPYRIGHT 2004 ACS on STN
ACCESSION NUMBER: 1985:471568 CAPLUS
DOCUMENT NUMBER: 103:71568
TITLE: A study of the phenolic oxidative coupling reaction in
the synthesis of morphine alkaloids
AUTHOR(S): Vanderlaan, Douglas George
CORPORATE SOURCE: Florida State Univ., Tallahassee, FL, USA
SOURCE: (1984) 105 pp. Avail.: Univ. Microfilms Int., Order
No. DA8428711
From: Diss. Abstr. Int. B 1985, 45(11), 3512
DOCUMENT TYPE: Dissertation
LANGUAGE: English
AB Unavailable
IT 57-27-2P, reactions 76-57-3P
RL: RCT (Reactant); SPN (Synthetic preparation); PREP
(Preparation); RACT (Reactant or reagent)
(formal synthesis of, via phenolic oxidative coupling)
RN 57-27-2 CAPLUS
CN Morphinan-3,6-diol, 7,8-didehydro-4,5-epoxy-17-methyl-,
(5 α ,6 α)- (9CI) (CA INDEX NAME)

Absolute stereochemistry. Rotation (-).



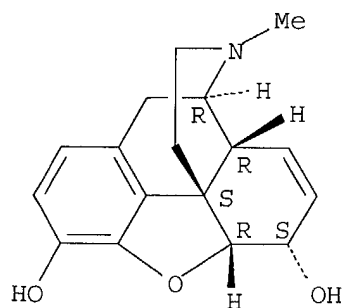
RN 76-57-3 CAPLUS
CN Morphinan-6-ol, 7,8-didehydro-4,5-epoxy-3-methoxy-17-methyl-,
(5 α ,6 α)- (9CI) (CA INDEX NAME)

Absolute stereochemistry.



L5 ANSWER 12 OF 16 CAPLUS COPYRIGHT 2004 ACS on STN
 ACCESSION NUMBER: 1984:139410 CAPLUS
 DOCUMENT NUMBER: 100:139410
 TITLE: Identification and determination of by-products of the codeine synthesis
 AUTHOR(S): Proksa, B.; Cerny, J.
 CORPORATE SOURCE: Slovakofarma, Hlohovec, 920 27, Czech.
 SOURCE: Chemicke Zvesti (1983), 37(6), 837-42
 CODEN: CHZVAN; ISSN: 0366-6352
 DOCUMENT TYPE: Journal
 LANGUAGE: English
 OTHER SOURCE(S): CASREACT 100:139410
 AB N,N,N',N'-Tetramethyl-4,4'-diaminodiphenylmethane, 6-methylcodeine, 17-norcodeine, α -codeimethine, and (3E)-O-dichlorovinylmorphine were found in the crude codeine obtained from morphine by methylation with trimethylphenylammonium hydroxide. A liquid-chromatog. method, employing column packed with reverse C-18-type phase, or alternatively gas-chromatog. one on XE-60/Chromaton N AW-DMCC were worked out for determination of these products.
 IT 57-27-2, reactions
 RL: **RCT (Reactant)**; RACT (Reactant or reagent)
 (methylation of, codeine from, byproducts from)
 RN 57-27-2 CAPLUS
 CN Morphinan-3,6-diol, 7,8-didehydro-4,5-epoxy-17-methyl- (5 α ,6 α) - (9CI) (CA INDEX NAME)

Absolute stereochemistry. Rotation (-).

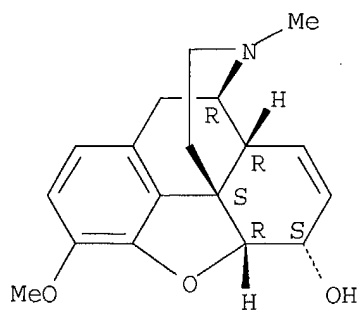


IT 76-57-3P
 RL: RCT (Reactant); **PREP (Preparation)**; RACT (Reactant or reagent)
 (synthesis of, by methylation of morphine, byproducts from)
 RN 76-57-3 CAPLUS
 CN Morphinan-6-ol, 7,8-didehydro-4,5-epoxy-3-methoxy-17-methyl-,

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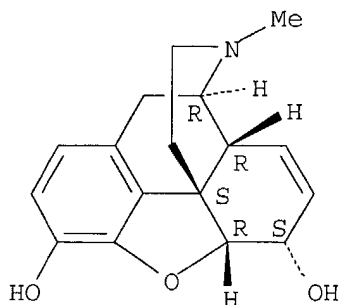
(5 α ,6 α)- (9CI) (CA INDEX NAME)

Absolute stereochemistry.



L5 ANSWER 13 OF 16 CAPLUS COPYRIGHT 2004 ACS on STN
ACCESSION NUMBER: 1980:514776 CAPLUS
DOCUMENT NUMBER: 93:114776
TITLE: Semisynthesis of codeine
AUTHOR(S): Tran Nguyen Huu; Bui Le My; Nguyen Lan Phuong; Nguyen Huu Dinh
CORPORATE SOURCE: Xi Nghiep Duoc Pham 2, Hanoi, Vietnam
SOURCE: Duoc Hoc (1979), (2), 21-2
CODEN: DCHCAM
DOCUMENT TYPE: Journal
LANGUAGE: Vietnamese
AB The semisynthesis of codeine (70-90% yield) was performed by methylation of morphine with a methylating agent obtained by ion exchange of a quaternary ammonium salt (TMC) prepared at room temperature TMC behaves similarly to PhMe₃N⁺ Cl⁻. Optimum conditions were found to stop the methylation reaction before the formation of thebaine.
IT 57-27-2, reactions
RL: **RCT (Reactant)**; RACT (Reactant or reagent)
(methylation of, to codeine)
RN 57-27-2 CAPLUS
CN Morphinan-3,6-diol, 7,8-didehydro-4,5-epoxy-17-methyl-
(5 α ,6 α)- (9CI) (CA INDEX NAME)

Absolute stereochemistry. Rotation (-).

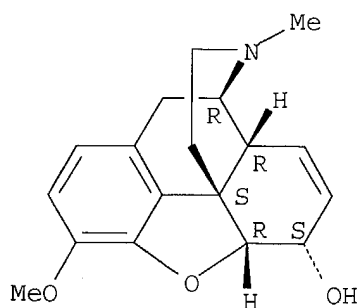


IT 76-57-3P
RL: SPN (Synthetic preparation); **PREP (Preparation)**
(semisynthesis of, by methylation of morphine)
RN 76-57-3 CAPLUS
CN Morphinan-6-ol, 7,8-didehydro-4,5-epoxy-3-methoxy-17-methyl-,

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(5 α ,6 α)- (9CI) (CA INDEX NAME)

Absolute stereochemistry.



L5 ANSWER 14 OF 16 CAPLUS COPYRIGHT 2004 ACS on STN
ACCESSION NUMBER: 1974:48216 CAPLUS
DOCUMENT NUMBER: 80:48216
TITLE: Selective methylating agent
INVENTOR(S): Sistare Noguera, Jose
PATENT ASSIGNEE(S): Union Quimico-Farmaceutica S.A.E.
SOURCE: Span., 6 pp.
CODEN: SPXXAD

DOCUMENT TYPE: Patent
LANGUAGE: Spanish
FAMILY ACC. NUM. COUNT: 1
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
ES 389682	A1	19730616	ES 1971-389682	19710329

PRIORITY APPLN. INFO.: ES 1971-389682 19710329

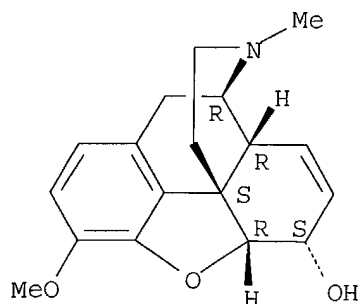
AB Morphine was treated with RN:C(OMe)NHR (I; R = alkyl, aryl) in MeOH to give codeine. I was prepared by reaction of RN:C:NR with MeOM (M = alkaline earth metal) in absolute MeOH.

IT **76-57-3P**
RL: IMF (Industrial manufacture); **PREP (Preparation)**
(manufacture of)

RN 76-57-3 CAPLUS

CN Morphinan-6-ol, 7,8-didehydro-4,5-epoxy-3-methoxy-17-methyl-,
(5 α ,6 α)- (9CI) (CA INDEX NAME)

Absolute stereochemistry.



IT **57-27-2**, reactions
RL: **RCT (Reactant)**; RACT (Reactant or reagent)

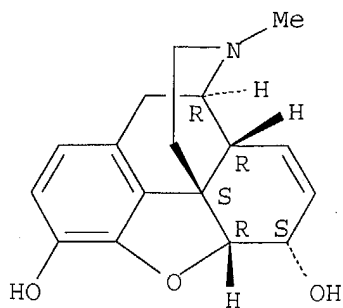
10/849,696

(methylation of, selective)

RN 57-27-2 CAPLUS

CN Morphinan-3,6-diol, 7,8-didehydro-4,5-epoxy-17-methyl-
(5 α ,6 α)- (9CI) (CA INDEX NAME)

Absolute stereochemistry. Rotation (-).



L5 ANSWER 15 OF 16 CAPLUS COPYRIGHT 2004 ACS on STN

ACCESSION NUMBER: 1973:537324 CAPLUS

DOCUMENT NUMBER: 79:137324

TITLE: Preparation of codeine by methylation of morphine with
phenyltrimethylammonium methoxide

AUTHOR(S): Ikononovski, Kostantin

CORPORATE SOURCE: S. B. Penick Co., Newark, NJ, USA

SOURCE: Acta Pharmaceutica Jugoslavica (1973), 23(3), 169-71
CODEN: APJUA8; ISSN: 0001-6667

DOCUMENT TYPE: Journal

LANGUAGE: English

GI For diagram(s), see printed CA Issue.

AB Morphine (I; R = H) reacted with PhMe₃N⁺ MeO⁻ in xylene-MeOH at
115° to give 98% codeine (I; R = Me).

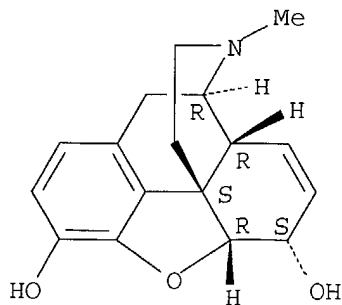
IT 57-27-2, reactions

RL: **RCT (Reactant)**; RACT (Reactant or reagent)
(methylation of, by trimethylphenylammonium methoxide)

RN 57-27-2 CAPLUS

CN Morphinan-3,6-diol, 7,8-didehydro-4,5-epoxy-17-methyl-
(5 α ,6 α)- (9CI) (CA INDEX NAME)

Absolute stereochemistry. Rotation (-).



IT 76-57-3P

RL: SPN (Synthetic preparation); **PREP (Preparation)**
(preparation of)

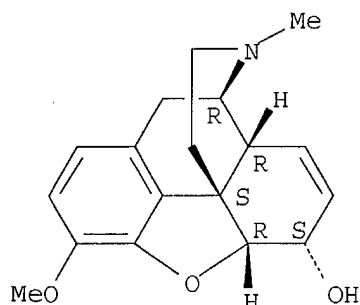
RN 76-57-3 CAPLUS

CN Morphinan-6-ol, 7,8-didehydro-4,5-epoxy-3-methoxy-17-methyl-,

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(5 α ,6 α) - (9CI) (CA INDEX NAME)

Absolute stereochemistry.



L5 ANSWER 16 OF 16 CAPLUS COPYRIGHT 2004 ACS on STN

ACCESSION NUMBER: 1972:501952 CAPLUS

DOCUMENT NUMBER: 77:101952

TITLE: Improvement in the technology of codeine synthesis from morphine

AUTHOR(S): Smirnov, D. M.; Sigal, E. L.; Marechek, K. Ya.; Zakharov, V. P.

CORPORATE SOURCE: Khim.-Farm. Zavod im. Dzerzhinskogo, Chimkent, USSR

SOURCE: Khimiko-Farmatsevticheskii Zhurnal (1972), 6(5), 31-6
CODEN: KHFZAN; ISSN: 0023-1134

DOCUMENT TYPE: Journal

LANGUAGE: Russian

AB Replacing PhMe as a solvent for the methylation of morphine using PhNMe₃OH with C₆H₄Me₂ enables one to perform the reaction at a lower temperature (102-5°, compared with 110-13°) in a shorter time (45 min instead of 90). A very pure codeine was obtained in a yield higher than 5%.

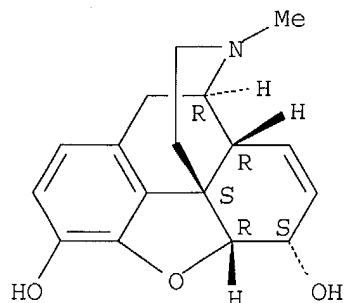
IT 57-27-2, reactions

RL: RCT (Reactant); RACT (Reactant or reagent)
(methylation of)

RN 57-27-2 CAPLUS

CN Morphinan-3,6-diol, 7,8-didehydro-4,5-epoxy-17-methyl-
(5 α ,6 α) - (9CI) (CA INDEX NAME)

Absolute stereochemistry. Rotation (-).



IT 76-57-3P

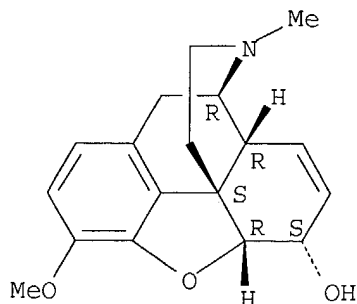
RL: RCT (Reactant); PREP (Preparation); RACT (Reactant or reagent)
(synthesis of)

RN 76-57-3 CAPLUS

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CN Morphinan-6-ol, 7,8-didehydro-4,5-epoxy-3-methoxy-17-methyl-,
(5 α ,6 α)- (9CI) (CA INDEX NAME)

Absolute stereochemistry.



=> d his

(FILE 'HOME' ENTERED AT 17:07:17 ON 19 OCT 2004)

FILE 'REGISTRY' ENTERED AT 17:08:31 ON 19 OCT 2004

L1 1 S CODEINE/CN
L2 1 S MORPHINE/CN

FILE 'CAPLUS' ENTERED AT 17:09:16 ON 19 OCT 2004

L3 120 S L1/PREP
L4 349 S L2/RCT
L5 16 S L3 AND L4

=> d l1

YOU HAVE REQUESTED DATA FROM FILE 'REGISTRY' - CONTINUE? (Y)/N:y

L1 ANSWER 1 OF 1 REGISTRY COPYRIGHT 2004 ACS on STN

RN 76-57-3 REGISTRY

CN Morphinan-6-ol, 7,8-didehydro-4,5-epoxy-3-methoxy-17-methyl-,
(5 α ,6 α)- (9CI) (CA INDEX NAME)

OTHER CA INDEX NAMES:

CN Morphinan-6 α -ol, 7,8-didehydro-4,5 α -epoxy-3-methoxy-17-methyl-
(8CI)

OTHER NAMES:

CN (-)-Codeine

CN **Codeine**

CN Codicept

CN Coducept

CN 1-Codeine

CN Methyilmorphine

CN Morphine 3-methyl ether

CN Morphine monomethyl ether

CN O3-Methyilmorphine

FS STEREOSEARCH

DR 120210-43-7, 79990-78-6

MF C18 H21 N O3

CI COM

LC STN Files: ADISNEWS, AGRICOLA, ANABSTR, BEILSTEIN*, BIOBUSINESS, BIOSIS,
BIOTECHNO, CA, CABA, CANCERLIT, CAOLD, CAPLUS, CASREACT, CBNB, CEN,
CHEMCATS, CHEMINFORMRX, CHEMLIST, CIN, CSCHEM, CSNB, DDFU, DETHERM*,

10/849,696

DIOGENES, DRUGU, EMBASE, GMELIN*, HODOC*, HSDB*, IFICDB, IFIPAT, IFIUDB, IMSCOSEARCH, MEDLINE, MRCK*, MSDS-OHS, NAPRALERT, NIOSHTIC, PROMT, PS, RTECS*, SPECINFO, TOXCENTER, USAN, USPAT2, USPATFULL, VETU

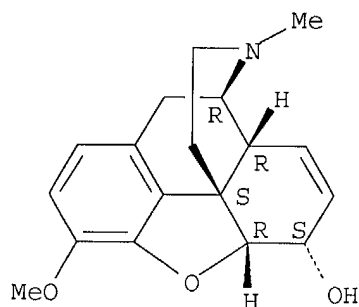
(*File contains numerically searchable property data)

Other Sources: EINECS**

(**Enter CHEMLIST File for up-to-date regulatory information)

DT.CA Caplus document type: Book; Conference; Dissertation; Journal; Patent; Report
RL.P Roles from patents: ANST (Analytical study); BIOL (Biological study); FORM (Formation, nonpreparative); MSC (Miscellaneous); OCCU (Occurrence); PREP (Preparation); PROC (Process); PRP (Properties); RACT (Reactant or reagent); USES (Uses); NORL (No role in record)
RLD.P Roles for non-specific derivatives from patents: ANST (Analytical study); BIOL (Biological study); PREP (Preparation); USES (Uses)
RL.NP Roles from non-patents: ANST (Analytical study); BIOL (Biological study); FORM (Formation, nonpreparative); MSC (Miscellaneous); OCCU (Occurrence); PREP (Preparation); PROC (Process); PRP (Properties); RACT (Reactant or reagent); USES (Uses); NORL (No role in record)
RLD.NP Roles for non-specific derivatives from non-patents: ANST (Analytical study); BIOL (Biological study); FORM (Formation, nonpreparative); OCCU (Occurrence); PREP (Preparation); PROC (Process); PRP (Properties); USES (Uses)

Absolute stereochemistry.



PROPERTY DATA AVAILABLE IN THE 'PROP' FORMAT

5103 REFERENCES IN FILE CA (1907 TO DATE)
66 REFERENCES TO NON-SPECIFIC DERIVATIVES IN FILE CA
5123 REFERENCES IN FILE CAPLUS (1907 TO DATE)
1 REFERENCES IN FILE CAOLD (PRIOR TO 1967)

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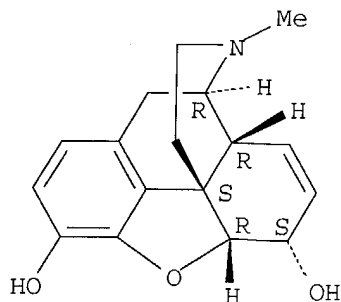
YOU HAVE REQUESTED DATA FROM FILE 'REGISTRY' - CONTINUE? (Y)/N:y

L2 ANSWER 1 OF 1 REGISTRY COPYRIGHT 2004 ACS on STN
RN 57-27-2 REGISTRY
CN Morphinan-3,6-diol, 7,8-didehydro-4,5-epoxy-17-methyl-
(5 α ,6 α)-(9CI) (CA INDEX NAME)
OTHER CA INDEX NAMES:
CN Morphinan-3,6 α -diol, 7,8-didehydro-4,5 α -epoxy-17-methyl- (8CI)
OTHER NAMES:
CN (-)-Morphine
CN Dulcontin
CN Duromorph

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CN 1-Morphine
CN Meconium
CN Morphia
CN Morphin
CN Morphina
CN **Morphine**
CN Morphinism
CN Morphinum
CN Morphium
CN MS Contin
CN Nepenthe
CN Ospalivina
FS STEREOSEARCH
DR 8053-16-5, 85201-37-2, 47106-99-0
MF C17 H19 N O3
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LC STN Files: ADISINSIGHT, ADISNEWS, AGRICOLA, ANABSTR, BEILSTEIN*,
BIOBUSINESS, BIOSIS, BIOTECHNO, CA, CABA, CANCERLIT, CAPLUS, CASREACT,
CBNB, CEN, CHEMCATS, CHEMINFORMRX, CHEMLIST, CIN, CSCHEM, CSNB, DDFU,
DETERM*, DIOGENES, DRUGU, EMBASE, GMELIN*, HODOC*, HSDB*, IFICDB,
IFIPAT, IFIUDB, IMSCOSEARCH, IPA, MEDLINE, MRCK*, MSDS-OHS, NAPRALERT,
NIOSHTIC, PHAR, PIRA, PROMT, PS, RTECS*, SPECINFO, TOXCENTER, USAN,
USPAT2, USPATFULL, VETU
(*File contains numerically searchable property data)
Other Sources: EINECS**
(**Enter CHEMLIST File for up-to-date regulatory information)
DT.CA Caplus document type: Book; Conference; Dissertation; Journal; Patent;
Report
RL.P Roles from patents: ANST (Analytical study); BIOL (Biological study);
FORM (Formation, nonpreparative); MSC (Miscellaneous); OCCU
(Occurrence); PREP (Preparation); PROC (Process); PRP (Properties); RACT
(Reactant or reagent); USES (Uses); NORL (No role in record)
RLD.P Roles for non-specific derivatives from patents: ANST (Analytical
study); BIOL (Biological study); PREP (Preparation); PROC (Process); PRP
(Properties); RACT (Reactant or reagent); USES (Uses)
RL.NP Roles from non-patents: ANST (Analytical study); BIOL (Biological
study); FORM (Formation, nonpreparative); MSC (Miscellaneous); OCCU
(Occurrence); PREP (Preparation); PROC (Process); PRP (Properties); RACT
(Reactant or reagent); USES (Uses); NORL (No role in record)
RLD.NP Roles for non-specific derivatives from non-patents: ANST (Analytical
study); BIOL (Biological study); FORM (Formation, nonpreparative); MSC
(Miscellaneous); OCCU (Occurrence); PREP (Preparation); PROC (Process);
PRP (Properties); RACT (Reactant or reagent); USES (Uses)

Absolute stereochemistry. Rotation (-).



10/849,696

PROPERTY DATA AVAILABLE IN THE 'PROP' FORMAT

24946 REFERENCES IN FILE CA (1907 TO DATE)

267 REFERENCES TO NON-SPECIFIC DERIVATIVES IN FILE CA

24977 REFERENCES IN FILE CAPLUS (1907 TO DATE)

=>

PALM INTRANET

Day : Tuesday
Date: 10/19/2004
Time: 16:47:52

Inventor Name Search Result

Your Search was:

Last Name = FRANCIS

First Name = CHARLES

Application#	Patent#	Status	Date Filed	Title	Inventor Name 23
60481270	Not Issued	159	08/20/2003	APPARATUS FACILITATING WALKING IN SKI BOOTS	FRANCIS, CHARLES JELINEK
60399226	Not Issued	159	07/25/2002	APPARATUS FACILITATING WALKING IN SKI BOOTS	FRANCIS, CHARLES JELINEK
60294470	Not Issued	159	05/30/2001	CONTACT LENS WITH PVA COVER LAYER	FRANCIS, CHARLES AUXILIUM
60257583	Not Issued	159	12/22/2000	CONTACT LENS WITH OPAQUE IRIS PATTERN	FRANCIS, CHARLES AUXILIUM
60107383	Not Issued	159	11/06/1998	METHOD TO IMPROVE CIRCULATION TO ISCHEMIC TISSUE	FRANCIS , CHARLES W
10892578	Not Issued	019	07/16/2004	PROCESS FOR MANUFACTURING OPIOID ANALGESICS	FRANCIS, CHARLES AUXILIUM
10850015	Not Issued	030	05/20/2004	PROCESS FOR THE PRODUCTION OF OPIATES	FRANCIS, CHARLES A.
10849696	Not Issued	030	05/20/2004	PROCESS FOR THE PRODUCTION OF OPIATES	FRANCIS, CHARLES A.
10813813	Not Issued	041	03/31/2004	PROCESS FOR MANUFACTURING THEBAINE	FRANCIS, CHARLES AUXILIUM
10692242	Not Issued	030	10/23/2003	PROCESS FOR PREPARING CODEINE	FRANCIS, CHARLES A.
10455202	Not Issued	092	06/05/2003	PROCESS FOR MANUFACTURING OXYCODONE	FRANCIS, CHARLES AUXILIUM

<u>10455197</u>	<u>6790959</u>	150	06/05/2003	PROCESS FOR MANUFACTURING THEBAINE	FRANCIS, CHARLES AUXILIUM
<u>10152942</u>	Not Issued	071	05/22/2002	CONTACT LENS WITH PVA COVER LAYER	FRANCIS, CHARLES AUXILIUM
<u>10017026</u>	Not Issued	161	12/14/2001	CONTACT LENS WITH OPAQUE IRIS PATTERN	FRANCIS, CHARLES AUXILIUM
<u>09435286</u>	Not Issued	041	11/05/1999	METHOD TO IMPROVE CIRCULATION TO ISCHEMIC TISSUE	FRANCIS , CHARLES W.
<u>09260098</u>	Not Issued	161	03/02/1999	THERAPEUTIC MATERIAL CONTAINING GROWTH FACTOR BOUND TO FIBRINOGEN OR TO FIBRIN	FRANCIS , CHARLES W.
<u>07499250</u>	<u>5206140</u>	150	03/26/1990	ASSAY FOR SOLUBLE CROSSLINKED FIBRIN POLYMERS	FRANCIS , CHARLES W.
<u>07366631</u>	<u>5024475</u>	250	06/05/1989	STRENGTHENING DOOR JAMB	FRANCIS , CHARLES E.
<u>07299791</u>	<u>4899416</u>	150	01/23/1989	WIND POWERED CLEANING AND POLISHING FLAP FOR BOAT RAILS	FRANCIS , CHARLES
<u>07213572</u>	Not Issued	161	06/24/1988	ASSAY FOR SOLUBLE CROSSLINKED FIBRIN POLYMERS	FRANCIS , CHARLES W.
<u>07197444</u>	<u>4865370</u>	150	05/23/1988	KEEPER FOR DEADBOLT LOCKS	FRANCIS , CHARLES E.
<u>06944933</u>	Not Issued	161	12/22/1986	KEEPER FOR DEADBOLT LOCKS	FRANCIS , CHARLES E.
<u>06800696</u>	Not Issued	161	11/22/1985	KEEPER FOR DEADBOLT LOCKS	FRANCIS , CHARLES E.

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